



PATENT
Attorney Docket No. 7392/71618

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

FITZ et al.

Application No.: 09/899,825

Filed: July 6, 2001

For: FLAVOUR PRECURSORS

September 28, 2001

CLAIM OF PRIORITY

Assistant Commissioner for Patents
Washington, D.C. 20231

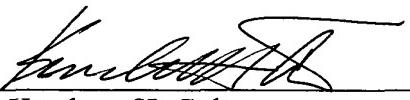
Dear Sir:

Submitted herewith in the above-identified application, through the undersigned attorney, Applicants hereby request that their above-identified application be treated as entitled to the right accorded by Title 35, U.S. Code, Section 119, having regard to the application, whereby certified copy of EP-00202431.3, filed 7 July 2000 of the priority document is enclosed.

Respectfully submitted,

FITCH, EVEN, TABIN & FLANNERY

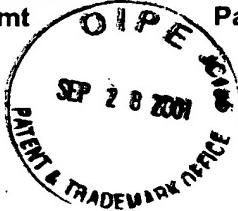
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Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00202431.3

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

Anmeldung Nr.:
Application no.: **00202431.3**
Demande n°:

Anmeldetag:
Date of filing: **07/07/00**
Date de dépôt:

Anmelder:
Applicant(s):
Demandeur(s):
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Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention:
Thiocarbonate as flavour precursors

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

Staat:	Tag:	Aktenzeichen:
State:	Date:	File no.
Pays:	Date:	Numéro de dépôt:

Internationale Patentklassifikation:
International Patent classification:
Classification internationale des brevets:
C07D307/38, A23L1/226

Am Anmeldetag benannte Vertragstaaten:
Contracting states designated at date of filing: AT/BE/CH/CY/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE/TR
Etats contractants désignés lors du dépôt:

Bemerkungen:
Remarks:
Remarques:

See for original title of the application page 1 of the description

Flavour precursors

The invention relates to flavour precursors, to foodstuffs containing one or more of such flavour precursors, to a process for flavouring foodstuffs by converting the 5 flavour precursors into the actual flavour compounds as well as to the use of the flavour precursors in the manufacture of foodstuffs and of foodstuff flavours.

Background of the Invention

10 There is a constant need for the enhancement and/or improvement of the flavour of foodstuffs like coffee etc.. Many relevant foodstuffs flavour compounds, like furfurylthiol are very unstable, i.e. will deteriorate rather quickly under the foodstuff preparing, storing and consuming conditions, resulting in an undesirable low and/or short flavour impression of the foodstuff to be consumed.

15 In this respect it is brought to the fore that sulfur flavour precursors are known in the art. For instance, US-A 3,978,240 already issued in 1976, relates to thiol precursors having the general formula $R_1-S-CO-O-R_2$, wherein R_1 is a substituted or unsubstituted alkyl, homo or heterocyclic radical having up to 10 carbon atoms and not more than two hetero atoms selected from the group consisting of oxygen and sulphur, and 20 wherein R_2 represents a secondary or tertiary hydrocarbyl group containing 3-20 carbon atoms, attached to the oxygen with the secondary or tertiary carbon atom. However, no indication whatsoever is given in said US-A 3,978,240 about the possible use of primary hydrocarbyl groups as examples for the meaning of R_2 . Apparently, the inventors of US-A 3,978,240 even intentionally excluded such primary hydrocarbyl 25 groups for R_2 .

Description of the Invention

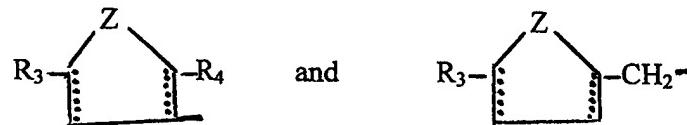
Surprisingly it has been found that a specific group of flavour precursors having 30 the formula



wherein

2

R₁ is a heterocyclic radical selected from the group consisting of



- wherein Z is an oxygen or a sulphur atom, R₃ and R₄ represent hydrogen or an C₁-C₄ alkyl group and the symbol —— represents a single or double bond,
10 and

- R₂ is derived from a group of primary alcohol compounds consisting of C₁-C₁₈ alkanols, glycerol and mono-, oligo- and polysaccharides, wherein the oxygen of the R₂-O- moiety is attached to a primary carbon atom of R₂
15 do have excellent properties in enhancing and imparting flavour to foodstuffs like coffee at the moment the foodstuff is prepared and/or consumed.

The invention therefore relates to flavour precursors having the formula



- 20 wherein R₁ and R₂ have the abovementioned meanings as defined in claim 1.

Detailed description of the invention

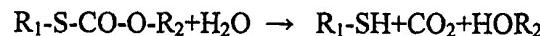
- 25 The flavour precursors according to the invention are characteristic for the following thiol or mercapto compounds from which the diester precursors can be prepared by one of the synthetic routes described below, the compounds are

- 4-mercaptop-5-methyl-tetrahydrofuran-3-one
- 30 4-mercaptop-2,5-dimethyl-tetrahydrofuran-3-one
- 3-mercaptop-2-methyl-tetrahydrofuran (cis and trans)
- 3-mercaptop-5-methyl-tetrahydrofuran (cis and trans)
- 3-mercaptop-5-methyl-tetrahydrothiophene (cis and trans)

- 3-mercaptop-2,5-dimethyl-tetrahydrothiophene
- 3-mercaptop-2-ethyl-5-methyl-tetrahydrothiophene
- 4-mercaptop-5-methyl-2,3-dihydrothiophene-3-one
- 4-mercaptop-2,5-dimethyl-2,3-dihydrofuran-3-one
- 5 3-mercaptop-2-methyl-4,5-dihydrofuran
- 3-mercaptop-2,5-dimethyl-4,5-dihydrofuran
- 3-mercaptop-2-methyl-2,3-dihydrothiophene
- 3-mercaptop-2,5-dimethyl-2,3-dihydrothiophene
- 3-mercaptop-2,5-dimethyl-2,3-dihydrofuran
- 10 3-mercaptop-5-ethyl-2,3-dihydrothiophene
- 3-mercaptop-2,5-dimethylfuran
- 3-mercaptop-2-methylfuran
- 3-mercaptop-5-methylfuran
- 3-mercaptop-2-ethylfuran
- 15 furfurylthiol
- 5-methylfurfurylthiol

Further, the invention relates to foodstuffs provided with one or more flavour precursors, generally present in an amount of 0,0001-100 ppm, preferably 0,001-20 ppm.

- A further aspect of the invention embraces the process for the flavouring of foodstuffs, i.e. enhancing or imparting the flavour by converting the flavour precursors in the foodstuffs at elevated temperature, for instance above 50°C, preferably 70-150°C, most preferably 90-130°C under normal or elevated pressure in an aqueous medium.
- 25 During said conversion of the precursors the desired flavour compounds and in principle harmless by-products are released. It is most likely that the conversion can be illustrated by the following equation:



30

wherein R₁SH represents the flavour compound, and R₂OH an alcohol.

The precursor compounds according to the invention can be prepared by methods known in the art. Two generally applicable methods are:

- (1) the conversion of chloroformic acid ester of the flavouring thiols with the formula R₁-S-COCl with the alcohols HOR₂ in the presence of a base;
or
(2) the conversion of the compound R₁X, wherein X represents a suitable halogen atom with an S-alkali metal salt of the thiocarbonic acid monoester of the alcohol HOR₂.

The foods in which the precursors (latent flavouring agents) have been incorporated are preferably to be heated before they are ready for consumption.

10 Foodstuffs according to the invention in which a flavour precursor has been incorporated are, for instance, dry, canned and frozen soups, ready meals, croquettes, sauce cubes, bouillon cubes, baking fats, margarine, bread, cakes, products simulating meat, as texturized vegetable protein, sterilized beverages such as sterilized coffee beverages, and instant drinks which are prepared with hot water, such as instant coffee.

15 The esters can be incorporated in the foodstuffs as such or dissolved or dispersed in a carrier, such as a fat, or enrobed with maltose-dextrin, gelatin, gum arabic. They can be mixed with the food ingredients ready to be prepared or mixed with one of the ingredients.

20 The flavour precursors incorporated in foodstuffs according to the invention may be used in conjunction with other substances useful for the required purpose. Thus it is possible to use coffee flavour precursors in conjunction with substances like milk products, both fresh milk, treated fresh milk and milk powder, sugar products like granulated sugar, sodium bicarbonate, emulsifiers like sucrose esters, stabilizing salts, antioxidants, hydrocolloids and coffee flavours per se.

25

Experimental

The invention will be illustrated by means of the following examples but should not be restricted thereto.

Example 1Preparation of O-ethyl S-(2-furylmethyl)thiocarbonate, (FFT-CO-OEt)

5 Furfurylthiol (527 g, 4.6 mol) and triethylamine (511 g, 5 mol) were added during a period of 6 hours at a temperature of 3-10°C to a solution of ethyl chloroformate (546 g, 5 mol) in methyl tert.butylether (MTBE) (2000 ml). The resulting mixture was stirred overnight and allowed to reach room temperature. Water (700 g) was added to the mixture to dissolve the triethylammonium chloride, which was formed during the
 10 reaction. Concentrated hydrochloric acid (70 g) was added to neutralise the excess triethylamine (TEAM). The organic layer was separated and washed with a saturated sodium hydrogen carbonate solution (1000 g) and water (1300 g). The organic layer was dried over magnesium sulphate and filtered. After evaporation of the solvent the crude product was distilled at 130-132°C at 30 torr to give 702 g (82%) O-ethyl S-(2-
 15 furylmethyl)thiocarbonate. The purity of the obtained product was determined by GC to be >99% and the structure was confirmed by NMR spectroscopy.

Reactionscheme:

Example 2

For the preparation of a sterilized coffee beverage the following procedure is followed:

(1)

- 5 (a) Weight out 45 g of coffee blend into a stainless steel container.
- (b) Add 25 g of water at 98°C to "steam the beans". Mix well and allow to stand for two minutes.
- (c) Add 450 g of deionised water (at 95°C) to the coffee blend, hold for 5 minutes with gentle stirring every 1.5 minutes (cover the container with aluminium foil).
- 10 (d) Pour the coffee solution into the "Kalita Coffee Filter" ensuring that all the coffee beans are added.
- (e) Collect the coffee extract and rinse the coffee beans in the filter three times with 60 g of deionised water at 95°C.
- (f) Add 50 g of granulated sugar to the coffee solution with stirring.

15

- 2) Add 0.8 g of NaHCO₃ to 50 g of deionized water at 90°C and stir until dissolved;
- 3) Add the NaHCO₃ solution to the coffee extract obtained above.
- 4) Slowly add 50 g of the milk ingredient to the coffee extract with gentle stirring.
- 20 5) Add 0.1 g of the coffee flavour^{*)} (2% soln) as well as 0.01 ppm of the coffee flavour precursor obtained in Example 1 and add water to bring solution to a mass of 1000 g.
- 6) Homogenize the solution with one pass through the Rannie homogenizer at 175 bar.
- 25 7) Cover the coffee beverage and heat it to 85°C. Fill it into cans and seal the cans.
- 8) Sterilize the cans at 121°C for 20 minutes.

*) The composition of the coffee flavour is as follows:

3,5-Dimethyl-2-ethylpyrazine	0.1
Acetylpyrzine	0.1
2,5-Dimethylpyrazine	0.2
3-Methylbutanal	0.6
Guaiacol	2
Cyclotene	4
Dimethylcyclopentanediol	2
Diacetyl	3
Acetylpropionyl	3
Ethylmethylpyrazine	4
2-Methoxy-4-vinylphenol	2
Butyric acid	10
Vanillin	4
Ethanol	rest.
Total	1000

A trained panel consisting of 11 evaluators compared the coffee sample prepared as described above to a coffee sample where no precursor was added. Eight out of the eleven evaluators preferred the coffee sample prepared as described above, as it showed an enhanced fresh coffee impression.

CLAIMS

EPO - DG 1

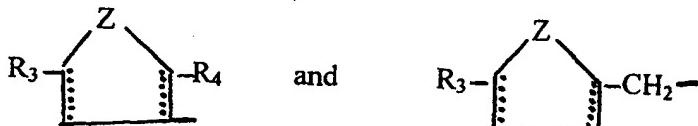
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5



(70)

wherein

 R_1 is a heterocyclic radical selected from the group consisting of

15 wherein Z is an oxygen or a sulphur atom, R_3 and R_4 represent hydrogen or an C_1 - C_4 alkyl group and the symbol ——— represents a single or double bond,
and

20 R_2 is derived from a group of primary alcohol compounds consisting of C_1 - C_{18} alkanols, glycerol and mono-, oligo- and polysaccharides, wherein the oxygen of the R_2-O- moiety is attached to a primary carbon atom of R_2

2. Flavour precursor according to claim 1, wherein the precursor is O-ethyl-S-(2-furylmethyl)thiocarbonate.

25 3. Foodstuff, provided with a flavour precursor according to claim 1 or 2.

4. Foodstuff, provided with 0.0001-100 ppm, preferably 0.001-20 ppm of a flavour precursor according to claim 1 or 2.

30 5. Process for the flavouring of foodstuffs by converting the flavour precursors according to claim 1 or 2, incorporated in the foodstuff according to claim 3 or 4 at an elevated temperature of from 70 to 150°C in an aqueous medium.

6. Use of the flavour precursors according to claim 1 or 2 in the manufacture of foodstuffs as well as foodstuff flavours.

ABSTRACT

5 The invention relates to flavour precursors having the formula

EPO - DG 1

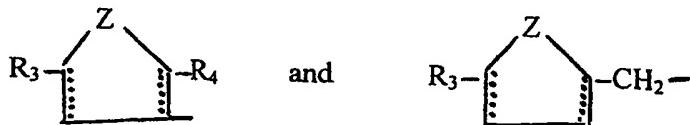
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(70)

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wherein Z is an oxygen or a sulphur atom, R_3 and R_4 represent hydrogen or an C_1-C_4 alkyl group and the symbol ——— represents a single or double bond,
and

20 R_2 is derived from a group of primary alcohol compounds consisting of C_1-C_{18} alkanols, glycerol and mono-, oligo- and polysaccharides, wherein the oxygen of the R_2-O- moiety is attached to a primary carbon atom of R_2

Further the invention relates to the foodstuffs provided with a flavour precursor
25 specified above.